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Relationship of ozone and carbon monoxide over North America

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Abstract. Observations at sites in eastern North America show a strong correlation between O_3 and CO concentrations in summer, with a consistent slope ΔO_3/ΔCO = 0.3. Observations in the aged Denver plume at Niwot Ridge, Colorado, also show a strong correlation but with ΔO_3/ΔCO = 0.15. These data offer a sensitive test for evaluating the ability of photochemical models to simulate production of O_3 over North America and its export to the global atmosphere. Application to the Harvard/Goddard Institute for Space Studies three-dimensional, continental-scale model shows that the model gives a good simulation of the observed O_3-CO correlations and of the associated ΔO_3/ΔCO. This successful simulation lends support to model estimates of 6 Gmol d^-1 for the net O_3 production in the U.S. boundary layer in summer (corresponding to a net O_3 production efficiency of 5.5, which is the number of O_3 molecules produced per molecule of NO_x consumed) and 70% for the fraction of the net production that is exported to the global atmosphere. Export of U.S. pollution appears to make a significant contribution to total tropospheric O_3 over the northern hemisphere in summer. Simple interpretation of observed ΔO_3/ΔCO as an O_3/CO anthropogenic enhancement ratio is shown to underestimate substantially anthropogenic O_3 production, because O_3 and CO concentrations are negatively correlated in the absence of photochemistry. It is also shown that concurrent observations of ΔO_3/ΔCO and ΔO_3/Δ(NO_x-NO_y) ratios can be used to impose lower and upper limits on the net O_3 production efficiency.

1. Introduction

Tropospheric O_3 is a key precursor of the hydroxyl radical which controls the oxidizing power of the atmosphere [Logan et al., 1981; Thompson, 1992]. Ozone is also one of the major pollutants which, in high concentration, can be harmful to human health and to plants. Large amounts of anthropogenic O_3 are produced over the United States in summer by photochemical oxidation of nonmethane hydrocarbons (NMHCs) in the presence of nitrogen oxides (NO_x = NO + NO_y). Quantifying this anthropogenic source of O_3 and assessing its global influence is presently a major research issue in tropospheric chemistry [Liu et al., 1987; International Global Atmospheric Chemistry (IGAC), 1992; Parrish et al., 1993].

The covariance of O_3 and CO concentrations offers a valuable constraint for quantifying the anthropogenic source of O_3. Carbon monoxide is a long-lived tracer of human activity with relatively well known sources from combustion, industry, and oxidation of hydrocarbons [Logan et al., 1981]. Several authors have used the O_3-CO correlation measured from aircraft downwind of the United States to diagnose pollution influence on O_3 [Fishman and Seiler, 1983; Fishman et al., 1987; Chameides et al., 1987, 1989; Marenco and Sait, 1989]. Recently, Parrish et al. [1993] made a first estimate of the export of anthropogenic O_3 from North America to the North Atlantic by using the slope ΔO_3/ΔCO = 0.3 measured at three Canadian marine sites downwind of the United States and scaling to a CO emission inventory for the eastern United States. They concluded that export of pollution from the United States dominates over transport from the stratosphere as a source of O_3 to the lower troposphere over the North Atlantic in summer.

A more detailed interpretation of ΔO_3/ΔCO in terms of O_3 production requires a three-dimensional model that can resolve complicating factors such as the effect of O_3 deposition, the presence of chemical sources and sinks for CO, and spatial variability. We present here such an analysis using a continental-scale model for O_3 and its precursors over North America [Jacob et al., 1993a]. Our principal objective is to use the O_3-CO correlation as a test of the ability of the model to compute production of O_3 over the continent. The particular value of this test is that it normalizes O_3 photochemical enhancements to a long-lived tracer of human activity. Ozone concentrations alone do not offer as sensitive a test because they include a substantial and variable background advected from the model boundaries (e.g., from the oceans or from high altitude). In rural surface
air over the eastern United States, about half of the mean summertime $O_3$ concentration appears to be contributed by advection from outside North America [Jacob et al., 1993a]. The $O_3$-CO correlation removes to a large degree the sensitivity to background. As such, it diagnoses whether the model is giving a successful simulation of $O_3$ for the right reasons.

Section 2 gives a brief description of the model and summarizes important previous results. Section 3 presents observed $O_3$-CO correlations at sites in North America and compares model to observations. Section 4 assesses the possibility for direct interpretation of observed $\Delta O_3/\Delta CO$ as an anthropogenic enhancement ratio. Conclusions are in section 5.

2. The Model

The three-dimensional photochemical model of Jacob et al. [1993a] covers a domain including North and Central America and important previous results. The $O_3$-CO correlations at sites in North America and compares model to observations. Section 4 assesses the possibility for direct interpretation of observed $\Delta O_3/\Delta CO$ as an anthropogenic enhancement ratio. Conclusions are in section 5.

The model reproduces the observed summer median $O_3$ concentrations to within 5 ppb in most cases, except in the south central United States where concentrations are overpredicted by 15–20 ppb due to insufficient ventilation. Median summertime concentrations of CO are simulated to within 30 ppb at all sites, and the spatial variance of rural CO across the United States is well captured.

A detailed discussion of the $O_3$ budget in the three-dimensional model is given by Jacob et al. [1993b]. The net production rate of $O_3$ in the U.S. boundary layer (0–2.6 km altitude) averages 6.1 Gmol d$^{-1}$ for the 3 month period June to August. The net $O_3$ production efficiency $\phi_N$ (net number of $O_3$ molecules produced per molecule of NOx consumed, as defined by Lin et al. [1988]) has a mean value of 5.5 in the U.S. boundary layer and is more than 2 times higher in the western United States (9.1) than in the east (4.2) because of lower NOx concentrations in the west. (Notice the slight changes of the values of $O_3$ production rate and net $O_3$ production efficiency from Jacob et al. [1993b], after correcting an error in saving those values.) Only 30% of the net $O_3$ production in the U.S. boundary layer in the model is deposited to the region; the remaining 70% is exported to the global atmosphere. This export amounts to about one fifth of
Table 1. O$_3$-CO Correlations at North American Sites in Summer

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Period</th>
<th>n</th>
<th>O$_3$, ppb</th>
<th>CO, ppb</th>
<th>ΔO$_3$/ΔCO, v/v</th>
<th>$r^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harvard Forest, Massachusetts</td>
<td>42°N, 72°W</td>
<td>June to Aug. 1990 - 1992</td>
<td>100</td>
<td>53</td>
<td>151</td>
<td>0.28 ± 0.02</td>
<td>0.78</td>
<td>J. Munger (unpublished data, 1993)</td>
</tr>
<tr>
<td>Scotia, Pennsylvania</td>
<td>41°N, 78°W</td>
<td>July to Aug. 1988</td>
<td>96</td>
<td>51</td>
<td>149</td>
<td>0.29 ± 0.02</td>
<td>0.81</td>
<td>D. Parrish et al. (unpublished data, 1980)</td>
</tr>
<tr>
<td>Kinterbishi, Alabama</td>
<td>32°N, 88°W</td>
<td>June to July 1990</td>
<td>28</td>
<td>60</td>
<td>172</td>
<td>0.32 ± 0.03</td>
<td>0.57</td>
<td>D. Parrish et al. (unpublished data, 1991)</td>
</tr>
<tr>
<td>Shenandoah National Park, Virginia</td>
<td>39°N, 79°W, 1100 m</td>
<td>June to Aug. 1989</td>
<td>155</td>
<td>41</td>
<td>206</td>
<td>a</td>
<td>0.09</td>
<td>Poulida et al. [1991]</td>
</tr>
<tr>
<td>Niwot Ridge, Colorado</td>
<td>40°N, 105°W, 3100 m</td>
<td>July to Aug. 1989</td>
<td>40</td>
<td>51</td>
<td>121</td>
<td>0.15 ± 0.02</td>
<td>0.50</td>
<td>D. Parrish et al. (unpublished data, 1990)</td>
</tr>
<tr>
<td>Seal Island, Canada</td>
<td>43°N, 66°W</td>
<td>July to Aug. 1991</td>
<td>527</td>
<td>36</td>
<td>118</td>
<td>0.25 ± 0.01</td>
<td>0.77</td>
<td>Parrish et al. [1993]$^c$</td>
</tr>
<tr>
<td>Sable Island, Canada</td>
<td>44°N, 60°W</td>
<td>July to Aug. 1991</td>
<td>1098</td>
<td>40</td>
<td>130</td>
<td>0.30 ± 0.01$^b$</td>
<td>0.63</td>
<td>Parrish et al. [1993]$^c$</td>
</tr>
<tr>
<td>Cape Race, Canada</td>
<td>47°N, 53°W</td>
<td>July to Aug. 1991</td>
<td>1035</td>
<td>38</td>
<td>123</td>
<td>0.31 ± 0.02$^b$</td>
<td>0.59</td>
<td>Parrish et al. [1993]$^c$</td>
</tr>
</tbody>
</table>

Observation statistics are computed from hourly average data; for flatland and mountaintop sites, only data in the time window of 1300-1700 LT and with NO$_x$/NO$_y$ < 0.3 are used (see text). Model statistics are computed from output sampled every 4 hours (model time step), in the 1300-1700 LT window for continental sites, and at all times of day at marine sites.

$^a$Observed O$_3$ and CO concentrations are not correlated.

$^b$Model correlations are computed for marine sites after removing points with O$_3$ less than 35 ppb and CO less than 120 ppb (background conditions), to focus on the pollution signal.

$^c$September data reported by Parrish et al. are not included in the statistics.

The cross-tropopause transport of O$_3$ over the entire northern hemisphere in summer implies that O$_3$ produced in the United States makes a significant contribution to tropospheric O$_3$ on the hemispheric scale.

3. O$_3$-CO Correlations

Table 1 summarizes observed and simulated O$_3$-CO correlation statistics for eight nonurban sites in North America where at least 1 month of observations are available in summer (June to August). Site locations are shown in Figure 1. For continental sites we restrict our attention to the 1300-1700 LT window, when surface air is most likely representative of the boundary layer. Such a restriction is not needed at marine sites where we use data for all times of day. The model gives one value per day in the 1300-1700 LT window at any site, the exact hour depending on longitude (1300 LT in Colorado, 1500 LT on the East Coast of the United States); we use that value for constructing model statistics. All statistics in the model are constructed for June to August ($n = 92$ points at continental sites; $n = 552$ points at marine sites), even when the observations cover only a fraction of that period.

Figure 2 plots observed O$_3$ versus CO concentrations at Harvard Forest in central Massachusetts. There is no significant correlation because of a number of points with elevated CO but low O$_3$, representing fresh pollution plumes that have not yet realized their O$_3$ production potential. Production of O$_3$ over the United States in summer is mostly NO$_x$ limited [Trainer et al., 1987; Sillman et al., 1990b; McKeen et al., 1991; Chameides et al., 1992]; therefore realization of the O$_3$ production potential can be diagnosed by the NO$_x$/NO$_y$ concentration ratio where NO$_y$ represents the sum of NO$_x$ and its oxidation products [Trainer et al., 1993]. Figure 3 plots the NO$_x$/NO$_y$ concentration ratio at Harvard Forest against the standard normal distribution. Two distinctly different populations are found: NO$_x$/NO$_y$ < 0.3 (photochemically aged rural air) and NO$_x$/NO$_y$ > 0.3 (fresh pollution). The rural air data (solid circles in Figure 2) show a strong correlation between O$_3$ and CO concentrations ($r^2 = 0.78$). This correlation is insensitive to small changes in the NO$_x$/NO$_y$ criterion (using NO$_x$/NO$_y$ < 0.2 as the criterion does not alter the correlation or the slope).

Figure 4 compares model results with rural observations (diagnosed by NO$_x$/NO$_y$ < 0.3) at the five flatland and mountaintop sites listed in Table 1. The sites were chosen for the availability of concurrent observations for O$_3$, CO, NO$_x$, and NO$_y$. The measurements at Shenandoah include NO and NO$_y$ concentrations but not NO$_x$ [Dodridge et al., 1992]; we estimate the NO$_x$ concentrations at that site from NO/NO$_x$/O$_3$ photooxidation steady state [Leighton, 1961], using local UV flux measurements to estimate the NO$_x$ photolysis rate constant [Madronich, 1987]. Selection of data with NO$_x$/NO$_y$ < 0.3 is not possible in the model because NO$_y$ is not a tracer; however, it is not necessary
Figure 2. Hourly averaged $O_3$ and CO concentrations measured at Harvard Forest, Massachusetts, in June to August, 1300–1700 EST, 1990–1992. Solid and open circles represent hourly periods with a $NO_2/NO_3$ concentration ratio less or greater than 0.3, respectively.

since urban and industrial pollution plumes are isolated in the model with the subgrid scheme.

The observations at Harvard Forest, Scotia (Pennsylvania), and Kinverbush (Alabama) show significant correlation between $O_3$ and CO concentrations, with $\Delta O_3/\Delta CO \sim 0.3$ at all three sites (Table 1). We find excellent agreement between model and observations at Harvard Forest for $O_3$ and CO concentrations and for the associated $\Delta O_3/\Delta CO$ (Figure 4a). The observations at Scotia are also well reproduced by the model, although the model has less scatter (Figure 4b). The model also reasonably agrees with the observations at Kinverbush; although the slope in the model is somewhat higher than in the observations (Figure 4c), they overlap within the standard error. The model does not, in general, capture the extremes in the observed concentrations, in part because of spatial averaging on the $4^\circ \times 5^\circ$ grid scale.

Results for Shenandoah National Park, Virginia (mountaintop site, 1100 m altitude) are shown in Figure 4d. The observations show no significant $O_3$-CO correlation, while the model shows a strong correlation with slope $\Delta O_3/\Delta CO \sim 0.3$. The median concentration of $O_3$ in the model is 22 ppb higher than observed, while the median concentration of CO is 30 ppb lower. Model statistics are for the lowest layer (0–500 m altitude) to account for the upslope circulation in the daytime [Poolda et al., 1991]; however, model results in layer 2 (corresponding to the actual altitude of the site) are not significantly different. The observations are from the summer of 1989, which was unusually cold, cloudy, and rainy; mean $O_3$ concentrations at the site that summer were 10 ppb lower than the average for the past six summers [Poolda et al., 1991].

Results for Niwot Ridge, Colorado (3100 m) are shown in Figure 4e. The observations at Niwot Ridge sample, in general, either relatively clean air advected from the west or boundary layer air transported upslope from the east and contaminated by the Denver metropolitan area [Parrish et al., 1990]. The $O_3$-CO correlation in the observations is driven by the Denver plume. We show in Figure 4e model results for air at the altitude of Niwot Ridge (open squares) and for the 4- to 8-hour old Denver plume resolved with the subgrid scheme (open triangles). Model results seem consistent with observations. We find that $\Delta O_3/\Delta CO$ at Niwot Ridge is markedly lower than at rural eastern U.S. sites, both in the observations and in the model (Table 1). This result can be explained by the low $NO_2/CO$ emission ratio in the Denver metropolitan area (0.14) as compared to the average for the eastern United States (0.23) [EPA, 1989]. The low $NO_2/CO$ emission ratio in Denver reflects the dominance of mobile sources and fuel-rich combustion in automobiles not tuned to the local altitude of 1600 m [Parrish et al., 1991].

Figure 5 compares model and observations at three Canadian marine sites [Parrish et al., 1993]. These sites are downwind of the northeastern United States in the prevailing summertime circulation [Wendland and Bryson, 1981]. The observations indicate $\Delta O_3/\Delta CO$ in the range of 0.21 to 0.30, similar to values at eastern U.S. sites (Table 1). Model results are in good agreement. The variance in the model is far less than observed, certainly in part because aged pollution plumes are forced to dilute on the $4^\circ \times 5^\circ$ grid scale (no cross-gridbox advection is allowed for subgrid plumes in the model).

Our analysis indicates that $\Delta O_3/\Delta CO \sim 0.3$ is a uniform characteristic of boundary layer air over eastern North America in summer. Data for the free troposphere from the Arctic Boundary Layer Expeditions (ABLE) 3A and 3B [Harriss et al., 1992, 1994] are generally consistent with this result. Wofsy et al. [1992] measured $\Delta O_3/\Delta CO$ in the range 0.17–0.62 at 3–6 km altitude during an ABLE 3A flight along the eastern seaboard from Maine to Virginia. They measured a negative $\Delta O_3/\Delta CO$ below 1.5 km on the same flight, evidently due to $O_3$ deposition. Data from ABLE 3B show $\Delta O_3/\Delta CO$ in the range 0.20–0.69 for anthropogenic pollution plumes sampled in the free troposphere over eastern Canada [Mauzeroll et al., 1993].

4. Interpretation

We have shown that the three-dimensional model of Jacob et al. [1993a] reproduces closely the $O_3$-CO correlation and slope $\Delta O_3/\Delta CO$ for all available sites in North America except Shenandoah National Park. This finding, combined with the generally good simulation of $O_3$ and CO concentra-

Figure 3. The $NO_2/NO_3$ concentration ratio measured at Harvard Forest (for the same time period as in Figure 2) plotted against the standard normal distribution.
tions, lends confidence in the ability of the model to compute anthropogenic production of O$_3$ over the United States and the export of O$_3$ to the global atmosphere. Detailed discussion of model results, including O$_3$ budgets, is given by Jacob et al. [1993b].

We evaluate here the potential for a more direct interpretation of $\Delta$O$_3$/\Delta CO as an O$_3$/CO anthropogenic enhancement

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**Figure 4.** Observed and simulated O$_3$ and CO concentrations at five U.S. sites: (a) Harvard Forest, Massachusetts; (b) Scotia, Pennsylvania; (c) Kinterbush, Alabama; (d) Shenandoah National Park, Virginia; and (e) Niwot Ridge, Colorado. Details of the data are given in Table 1. Solid circles are observations and open squares are model values. In Figure 4e, model results are shown also for the aged Denver plume sampled with the sub-grid-nested scheme (open triangles). Lines are linear regressions to the observations (solid) and to the model results (dashed).

ratio. Parrish et al. [1993] previously used this interpretation to estimate the export of O$_3$ from the United States to the North Atlantic. They multiplied the observed $\Delta$O$_3$/\Delta CO = 0.3 at the Canadian marine sites of Table 1 by a CO emission inventory for the United States east of Mississippi River (approximately east of 92°W) and inferred an export flux of 1.1 Gmol d$^{-1}$ for anthropogenic O$_3$ out of the eastern United States (mostly, they assumed, to the North Atlantic). We find however in the model an export flux of 1.6 Gmol d$^{-1}$ for anthropogenic O$_3$ out of the same region; this flux is 45% higher than estimated by Parrish et al. [1993], even though $\Delta$O$_3$/\Delta CO in the model is indistinguishable from the observations. There are two principal reasons for the difference, as discussed below.

First, the scaling of $\Delta$O$_3$/\Delta CO as done by Parrish et al. [1993] could be improved by accounting for chemical sources and sinks of CO in addition to direct emission. Table 2 gives an inventory of CO sources and sinks for the continental boundary layer of the eastern United States in the three-dimensional model. Direct emission represents only 60% of the total CO source; the balance is contributed by atmospheric oxidation of hydrocarbons, in particular isoprene (20%). This chemical source is compensated by a strong chemical loss, reflecting the high concentrations of both CO and OH over the eastern United States. Overall, the net source of CO in the boundary layer of the eastern United States is 18% higher than the emission flux.

A more fundamental difficulty in interpreting observed $\Delta$O$_3$/\Delta CO as an O$_3$/CO anthropogenic enhancement ratio is that in the absence of photochemistry, O$_3$ would be nega-
Figure 5. Observed and simulated O$_3$ and CO concentrations at three Canadian marine sites (Table 1). Lines are linear regressions.

tively correlated with CO due to deposition. As a result, the measured $\Delta$O$_3$/rACO is less than the actual anthropogenic enhancement ratio. We determined the magnitude of this effect by conducting a model simulation with O$_3$ concentrations regulated solely by advection of boundary conditions and deposition (no chemical production or loss). Figure 6 shows the results for Seal Island, Canada; without photochemistry, O$_3$ and CO concentrations are negatively correlated (crosses, top panel). We can define an O$_3$ photochemical enhancement as the difference between the O$_3$ concentrations in the standard simulation and those in the simulation including no chemistry. This photochemical enhancement of O$_3$ shows a strong positive correlation with CO (solid squares, bottom panel). The slope in the bottom panel (0.40) gives the actual O$_3$/CO enhancement ratio from U.S. pollution; it is 33% higher than $\Delta$O$_3$/ACO in the top panel (0.30).

We now turn to the application of $\Delta$O$_3$/ACO as a measure of the O$_3$ production efficiency. Liu et al. [1987] pointed out that the O$_3$ production is best referenced to the loss of NO$_x$ or, on a regional scale, the emission of NO$_x$, since O$_3$ production is NO$_x$ limited. A net O$_3$ production efficiency $\eta_N$ was defined by Lin et al. [1988] as the net number of O$_3$ molecules produced per NO$_x$ molecule consumed. By scaling the observed $\Delta$O$_3$/ACO in photochemically aged air to a CO/NO$_x$ source ratio, we can obtain an estimate of the net O$_3$ production efficiency $\eta_N$; such an estimate is however a lower limit because of deposition of O$_3$. The CO/NO$_x$ source
ratio for the eastern United States, as defined in Figure 1, is 3.6 (using the net CO source in Table 2 and the NAPAP emission inventory for NOx). From $\Delta$O$_3$/ΔCO = 0.3, we obtain a net O$_3$ production efficiency $\varepsilon_N$ of 1.7 in eastern U.S. boundary layer. In comparison a value of 8.5 for $\varepsilon_N$ at Scotia and at Egbert, Ontario, was estimated by Trainer et al. [1993] using observations of $\Delta$O$_3$/Δ(NO$_2$-NO$_x$). Olszyna et al. [1993] found a $\varepsilon_N$ value of 12 at Tennessee using the same relationship; these values would be upper limits for $\varepsilon_N$ because of rapid HNO$_3$ deposition. Our three-dimensional model gives a mean value $\varepsilon_N$ = 4.2 for the eastern United States [Jacob et al., 1993b], which is intermediate between the lower and the upper limits imposed by the observations of $\Delta$O$_3$/ΔCO and $\Delta$O$_3$/Δ(NO$_2$-NO$_x$).

We have seen that deposition of O$_3$ is an important factor limiting the potential for simple interpretation of the O$_3$-CO correlation in terms of O$_3$ production. Model results indicate that this effect is greatest in the central United States, where O$_3$ concentrations would be at a minimum in the absence of photochemistry because of the long fetch in the continental boundary layer [Jacob et al., 1993a]. Figure 7 shows O$_3$-CO correlations for the Oregon, Nebraska, Illinois, and Massachusetts grid boxes; there is no significant correlation between O$_3$ and CO in the Nebraska grid box. By subtracting the O$_3$ concentration computed in the absence of photochemistry (as in Figure 6), we obtain a strong correlation between O$_3$ photochemical enhancement and CO (solid squares in Figure 7). The slope of the linear regression analysis of the O$_3$ photochemical enhancement versus CO falls within a narrow range (0.33 to 0.49) for the four grid boxes in Figure 7 and is actually highest in the Nebraska grid box.

5. Conclusion

Observations at nonurban sites in eastern North America show a strong correlation between O$_3$ and CO concentrations in photochemically aged air (as defined by NO$_2$/NO$_x$ < 0.3). The slope, $\Delta$O$_3$/ΔCO, has a remarkably uniform value of about 0.3. Observations at Niwot Ridge, Colorado, indicate $\Delta$O$_3$/ΔCO = 0.15 in the aged Denver plume; this low value is attributed to the low NO$_2$/CO emission ratio in the Denver metropolitan area.

The O$_3$-CO relationship provides a sensitive test of O$_3$ production in chemical transport models. We used it to test a three-dimensional, continental-scale model of O$_3$ and precursors over North America [Jacob et al., 1993a]. The model captures successfully the O$_3$-CO correlations and reproduces closely the observed $\Delta$O$_3$/ΔCO. It does not capture the full extent of variance in the observations, certainly in part because of spatial averaging on the grid scale. Simulation of the O$_3$-CO relationship lends confidence in the ability of the model to compute photochemical production of O$_3$ over North America and its export to the global atmosphere [Jacob et al., 1993b].

We investigated the possibility for a more direct interpretation of observed $\Delta$O$_3$/ΔCO as an O$_3$/CO anthropogenic enhancement ratio, to be multiplied by a CO source estimate for quantitative inference of photochemical O$_3$ production and export. A first complication with this simple approach is the need to account for chemical sources and sinks of CO, even in a highly polluted region such as the eastern United States. A second complication is that O$_3$ concentrations over polluted regions include a major component advected from outside the region, which is negatively correlated with CO due to deposition at the surface. As a result, $\Delta$O$_3$/ΔCO measured at sites over the United States and downwind is

Table 2. Budget of CO for the Boundary Layer of the Eastern United States

<table>
<thead>
<tr>
<th>Source/Reaction</th>
<th>Rate, Gmol d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic emission</td>
<td>3.3</td>
</tr>
<tr>
<td>Oxidation of isoprene</td>
<td>1.1</td>
</tr>
<tr>
<td>Oxidation of anthropogenic NMHCs</td>
<td>0.5</td>
</tr>
<tr>
<td>Oxidation of CH$_4$</td>
<td>0.6</td>
</tr>
<tr>
<td>Reaction with OH</td>
<td>-1.6</td>
</tr>
<tr>
<td>Net CO source</td>
<td>3.9</td>
</tr>
</tbody>
</table>

This budget is based on model results from June to August for the region enclosed by thick lines in Figure 1. Anthropogenic emission is from the National Acid Precipitation Assessment Program inventory. NMHCs, nonmethane hydrocarbons.
Figure 7. Simulated O₃ and CO concentrations in June to August (1200–1500 LT) for the Oregon, Nebraska, Illinois, and Massachusetts surface grid boxes. The open squares show O₃ concentrations from the standard simulation; the solid squares show the O₃ photochemical enhancement. The slopes and correlations for standard O₃ versus CO are Oregon, slope = 0.22, r² = 0.53; Nebraska, no significant correlation (r² = 0.15); Illinois, slope = 0.31, r² = 0.61; and Massachusetts, slope = 0.29, r² = 0.81. The slopes and correlations for the O₃ photochemical enhancement versus CO are Oregon, slope = 0.39, r² = 0.74; Nebraska, slope = 0.49, r² = 0.74; Illinois, slope = 0.33, r² = 0.60; and Massachusetts, slope = 0.39, r² = 0.87.

significantly less than the O₃/CO anthropogenic enhancement ratio, and the direct interpretation of observed ΔO₃/ΔCO may underestimate substantially the O₃ production and export.

From the ΔO₃/ΔCO observed in the eastern United States scaled to a CO/NOₓ source ratio for the region, we infer a lower limit of 1.7 for the net O₃ production efficiency ε₅N defined as the net number of O₃ molecules produced per molecule of NOₓ consumed. This value is a lower limit because of O₃ deposition. Observations of ΔO₃/Δ(NOₓ-NO₂) in the eastern United States yield values of 8.5–12 for ε₅N; these values are upper limit because of rapid HNO₃ deposition. The mean ε₅N value of 4.2 computed in the three-dimensional model for the boundary layer of the eastern United States falls within the limits imposed by the observations of ΔO₃/ΔCO and ΔO₃/Δ(NOₓ-NO₂).

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